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Reclaiming the spent alkaline zinc manganese dioxide batteries collected from the manufacturers to prepare valuable electrolytic zinc and LiNi$_{0.5}$Mn$_{1.5}$O$_4$ materials

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A B S T R A C T

A process for reclaiming the materials in spent alkaline zinc manganese dioxide (Zn–Mn) batteries collected from the manufacturers to prepare valuable electrolytic zinc and LiNi$_{0.5}$Mn$_{1.5}$O$_4$ materials is presented. After dismantling battery cans, the iron cans, covers, electric rods, organic separator, label, sealing materials, and electrolyte are separated through the washing, magnetic separation, filtrating, and sieving operations. Then, the powder residues react with H$_2$SO$_4$ (2 mol L^{-1}) solution to dissolve zinc under a liquid/solid ratio of 3:1 at room temperature, and subsequently, the electrolytic Zn with purity of ⩾99.8% is recovered in an electrolytic cell with a cathode efficiency of ⩾85% under the conditions of 37–40 °C and 300 A m^{-2}. The most of MnO$_2$ and a small quantity of electrolytic MnO$_2$ are recovered from the filtration residue and the electrodeposit on the anode of electrolytic cell, respectively. The recovered manganese oxides are used to synthesize LiNi$_{0.5}$Mn$_{1.5}$O$_4$ material of lithium-ion battery. The as-synthesized LiNi$_{0.5}$Mn$_{1.5}$O$_4$ discharges 118.3 mAh g^{-1} capacity and 4.7 V voltage plateau, which is comparable to the sample synthesized using commercial electrolytic MnO$_2$. This process can recover the substances in the spent Zn–Mn batteries and innocuously treat the wastewaters, indicating that it is environmentally acceptable and applicable.

1. Introduction

Zinc–manganese dioxide (Zn–Mn) batteries have been popularly used as the power sources in many electric appliances, including remote devices, camera, clock, toys, and so on. Hereinto, China, as the most important battery manufacturing area in the world, is currently annually producing over 20 billion pieces of Zn–Mn batteries. Correspondingly, the same amount of spent Zn–Mn batteries, in which contain Zn, Mn, Cu, and Fe elements along with a corrosive electrolytic solution, will be discarded as waste after their lifespan (Espinosa et al., 2004; Han and Nan, 2005; Sayilgan et al., 2009). In particular, these disposable batteries constitute a major waste stream of metallic compounds into landfill and can be a source of metal pollution in landfill leachate. Thus, dealing with the recycling of spent Zn–Mn batteries has become an urgent matter from the viewpoint of environmental preservation,

resource savings, and waste volume reduction (Nan et al., 2006a, 2006b, 2006c; Krekeler, 2008).

Besides the batteries collected from the consumers, those spent Zn–Mn batteries produced in the factories are an important waste source that cannot be ignored. Because the annual production quantity of each Zn–Mn battery factory is usually over a hundred million pieces, the amounts of these co-produced spent batteries in the manufacturing lines are too large to be neglected, although the drawback ratio is typically lower than 1%. In addition, the spent batteries backtracked from the shopkeepers to the manufacturers due to the reason of quality problem or quality guarantee period, even the spent batteries from the stockpile of manufacturer themselves, are all spent Zn–Mn battery sources. In practice, there are largish quantities of these mentioned spent Zn–Mn batteries. Therefore, the spent Zn–Mn batteries collected from the battery manufacturers should be severely considered. Because these spent Zn–Mn batteries have unambiguous substance compositions and low discharge levels, unlike other spent batteries collected as a waste from the consumers, it is necessary to investigate recycling methods with higher economic and usefulness to reclaim the valuable materials in these spent batteries.

The recycling methods of spent Zn–Mn batteries, which were usually summarized as pyrometallurgical and hydrometallurgical processes, have been extensively investigated to recover the valuable materials and eliminate the mercury pollution (Han and Nan, 2005; Sayilgan et al., 2009; Belardi et al., 2012). Up to the end of the last century, mercury was an essential additive in the manufacture of Zn–Mn batteries, especially for Zn–Mn dry batteries. Thus, the separation of mercury was emphasized as a key step in the early proposed methods, and the vacuum-aided recycling system was usually used to improve the volatilization and separation ratio of mercury and zinc from manganese at high temperature (Saotome et al., 1999; Oliveira et al., 2001; Belardi et al., 2014). Mercury and zinc could be reclaimed completely by using a pyrometallurgical process, but more energy was required and large-scale recycling was an economic possibility (Saotome et al., 1999; Oliveira et al., 2001; Peng et al., 2008; Kuo et al., 2009). In contrast, for those methods that combined with or based on hydrometallurgical process, e.g., the electrolysis (Vatistas et al., 2001; Freitas and Pietre, 2004; Souza and Tenório, 2004; Buzatu et al., 2013), solvent extraction (Salgado et al., 2003; El-Nadi et al., 2007; Baba et al., 2009; Hu et al., 2011), leaching-precipitation (Sayilgan et al., 2009; Shin et al., 2009; Kim et al., 2009), and other integrated methods (Espinosa et al., 2004; Han and Nan, 2005; Sayilgan et al., 2009; Belardi et al., 2012), the valuable substances contained in spent Zn–Mn batteries could be reclaimed into their respective parts, although these methods involve more steps and generate a large amount of waste solutions that require treatment. Moreover, compared to those simple recoveries of zinc or manganese substances, using spent Zn–Mn batteries as raw materials to directly synthesize functional materials demonstrates their superiority from the viewpoint of economics. For example, Zn–Mn ferrites have been synthesized by using the manganese, zinc and iron contained in spent Zn–Mn batteries as precursors (Han and Nan, 2005; Hu et al., 2011; Xiao et al., 2009; Gabal et al., 2013); Tu and co-authors used spent Zn–Mn dry battery to prepare the nano-adsorbents for hazardous metals removal (Tu et al., 2013).

Recently, only the Zn–Mn batteries without mercury additive have been supplied in the market, due to the increasing attention on the environmental preservation and the advances of the manufacturing technologies of the Zn–Mn batteries. Therefore, facile recycling methods without the treatment of mercury are expected to be required. In fact, the detailed steps for the proposed recycling methods are dependent on several factors, such as the source, composition, and charge status of the Zn–Mn batteries. Based on the previous advancements on the recycling of spent batteries (Han and Nan, 2005; Nan et al., 2006a, 2006b, 2006c), a batch of spent alkaline Zn–Mn batteries collected from a manufacture factory was treated in our lab. After dismantling the batteries, the magnetic iron cans, corrosive electrolyte, and valuable zinc and manganese compounds were separated into their respective parts. It was observed that although the manganese oxides, including the separated MnO_2 and the electrolytic MnO_2, could be obtained, how to use these manganese oxides and upgrade the reclaiming value must be considered because they had different particle size and pile-density compared to the commercial electrolytic MnO_2 and could not be directly used. Based on this situation, we tried to use the recovered manganese oxides as raw materials to synthesize lithium nickel manganese oxide ($LiNi_{0.5}Mn_{1.5}O_4$) cathode material. As a transition-metal-substituted spinel compound, $LiNi_{0.5}Mn_{1.5}O_4$ is a promising and attractive electrode material because of its good cyclic property and relatively high capacity with a plateau at approximately 4.7 V. In this paper, a process to reclaim the zinc and manganese elements to produce valuable electrolytic zinc and $LiNi_{0.5}Mn_{1.5}O_4$ battery material is presented.

2. Materials and methods

2.1. Materials and chemicals

The spent mercury-free AA size alkaline Zn–Mn batteries used in this work were kindly provided by GBW Battery Co. Ltd. These batteries were discarded as useless in the battery product line due to low voltage, zero voltage, or irregular appearance. The substances contained in these spent batteries were similar to those same type batteries in the market. The analysis indicated that a single cell weighed an average of 23.4 g, including approximately 4.6 g iron, 10.5 g MnO_2, 5.1 g zinc, 1.5 g KOH, 0.8 g organic materials (separator, label, and plastic cap), and 0.9 g of other materials, such as copper, carbon, and binders. Other chemicals and materials used in this works, including H_2SO_4, $Ni(OH)_2$, Li_2CO_3, metal lithium, and organic electrolyte, were all of battery grade and were used as received.

2.2. Reclamation procedure

Based on the components of spent Zn–Mn batteries and the pre-experimental investigation, a series of tests for defining the recycling steps were performed. The flow chart to reclaim the valuable materials, i.e., zinc, manganese, electrolyte, and iron, from the spent Zn–Mn batteries is presented in Fig. 1.

According to the flow chart presented in Fig. 1, the outer iron cans of batteries were firstly dismantled to favor separating the inner target substances in the succeeding steps, and then after the separation of iron, organic materials, and electrolyte, the high valuable residues were left for further recovery. Afterwards, the zinc and zinc compounds were dissolved into the acidic solution from the valuable residues and subsequently recovered through an electrodeposit method on the cathode of an electrolytic cell, while the most of MnO_2 is left as the filter residue, the small amount of dissolved manganese in the solution was recovered as the electrolytic MnO_2 on the anode of the electrolytic cell. Finally, the recovered manganese oxides were used as the manganese source to synthesize $LiNi_{0.5}Mn_{1.5}O_4$ material of lithium-ion battery via a solid-state reaction (Fang et al., 2006; Wu et al., 2009). In a typical process, stoichiometric amounts of the reclaimed manganese compounds, $Ni(OH)_2$, and Li_2CO_3 were mixed and thoroughly ball-milled, and the mixture was pressed into sheets and preheated at 700 °C for 3 h in air atmosphere. And then, the pre-
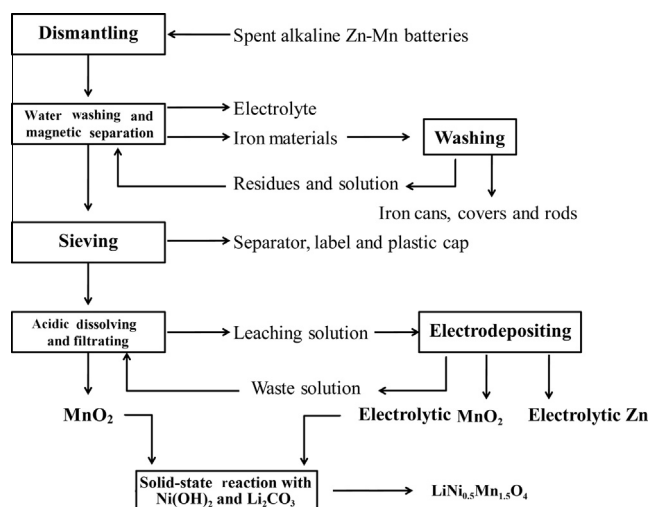

Fig. 1. Flow chart of the recycling of valuable materials from spent alkaline Zn–Mn batteries.

heated sample was successively ball-milled, pressed into sheets, and heated at 900 °C for 10 h. Next, after completion of carbon coating using 2% glucose as the carbon source at 600 °C in air for 3 h, the $LiNi_{0.5}Mn_{1.5}O_4$ cathode material of lithium-ion battery was obtained.

2.3. Instruments and analysis methods

The contents of metals in the acidic solutions and products were determined using an atomic absorption spectrophotometer (model AA320, Persee, China). The phase structures of the recovered materials were identified using powder X-ray diffraction (XRD; D/Max-IIIA, Rigaku, Japan) with Cu Kα radiation ($\lambda = 0.154$ nm) at 30 kV and 30 mA. The morphology of the samples was characterized by field emission scanning electron microscopy (FE-SEM; ZEISS ULTRA 55, Germany).

The electrodeposition experiments of metal zinc and manganese oxides from the zinc and manganese solution were performed in an electrolytic cell using an aluminum plate and a lead plate as the working electrode and the auxiliary electrode, respectively. Before the electrodeposition operation, one face of the two electrodes was sealed with epoxy resin, while the other face was pre-polished with sand paper and thoroughly rinsed with distilled water in an ultrasonic bath. The electrodeposition current was supplied by a galvanostatic instrument (Land, China).

The galvanostatic charge–discharge performances of the $LiNi_{0.5}$-$Mn_{1.5}O_4$ sample were evaluated on a multi-channel battery-testing unit (NEWARE CT-3008 W, China) using a coin-type cell (CR-2032) assembled using metal lithium sheet as anode and $LiNi_{0.5}Mn_{1.5}O_4$ electrode as cathode. The $LiNi_{0.5}Mn_{1.5}O_4$ electrode was prepared by coating the slurry of a mixture composed of 80 wt.% $LiNi_{0.5}$-$Mn_{1.5}O_4$, 10 wt.% conducting agent (Super-p), and 10 wt.% binder (polyvinylidene fluoride) onto an aluminum foil. After drying in air at 80 °C for 4 h, the electrode was pressed under 20 MPa for 1 min, and then dried at 120 °C for 24 h in a vacuum drier. The diameter of the electrode was 10 mm. The weight of active material in the electrode was 3.0 mg cm^{-2}. Afterwards, the coin-type cells were assembled in argon gas-filled glove box. The electrolyte was 1 mol L^{-1} LiPF$_6$ in the mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) with a volume ratio of 1:2. A polypropylene film (Cellgard 2300) was used as the separator. The cells were charged and discharged over a voltage range of 3.5–4.9 V versus Li/Li$^+$ electrode at room temperature.

3. Results and discussion

3.1. Separation of iron, organic materials, and electrolyte

The most valuable materials, i.e., Zn, MnO$_2$, and KOH electrolyte, are contained in the inner part of the spent batteries. To separate these materials, the outer iron cans must be firstly dismantled, and then the metallic materials (cans, covers, and negative current collector rods), electrolyte, and organic materials (separator, label, and sealing materials) could be separated. A specially designed dismantling machine, the working mechanism of which was expatiated in our other papers (Nan et al., 2006a, 2006b), was used to perform the dismantling work. The digital image of the dismantled substances is shown in Fig. 2a. It is clearly shown that the outer iron cans were mangled and that the inner substances were exposed after the dismantling operation.

The dismantled substances were poured into a plastic container, and a water washing treatment was performed to separate the KOH electrolyte. The corrosive electrolyte was washed out and concentrated by evaporation. During the water washing treatment, the inner substances of spent batteries could be peeled off from the

iron cans and the electric rods using sharp mechanical stirring for 30 min, which was appropriate for the next separating operation. The iron cans, cover, and electric rods were separated by using a magnet-like plate in the wet condition. The small quantity of powders left on the iron materials could also be watered out and then added into the remainder residues. The organic separator, label, and sealing materials were separated easily from the powder residues using a sieve with 1.5 mm apertures. The digital images of the separated materials are shown in Fig. 2b–e. Some powders left on the organic materials could also be washed out, afterwards, a dissolving treatment using hydrochloric acid must be performed to achieve complete separation. In the above steps, approximately 0.25×10^{-3} m^3 of water was required for 1 kg of dismantled substances.

3.2. Acidic leaching and zinc electrodeposition

After the separation of the iron cans, covers and electric rods, and the organic separator, label and sealing materials, the target valuable residues, i.e., metal zinc and zinc and manganese compounds, were left as powders. An ideal way to reclaim zinc and MnO$_2$ from the powder residues would be through preparing electrolytic zinc and MnO$_2$ on two electrodes of the electrolytic cell after the separation of iron and other impurities. However, the synchronous electrolysis of zinc and MnO$_2$ on two electrodes were restricted by their electrolytic requirements on the temperature, current density, solution concentration (Brito et al., 2012), and so on. Because these batteries were discarded as wastes in the battery product lines due to low voltage, zero voltage, or irregular appearance, the most of MnO$_2$ present in the original paste still exists as MnO$_2$ in the residue, and only metal zinc and zinc compounds are soluble components in H$_2$SO$_4$ solution with suitable concentration. Thus, the different leaching properties of MnO$_2$ and zinc in H$_2$SO$_4$ solution were utilized to separate them.

During the leaching treatment, the metal zinc and zinc compounds in the powder residues were dissolved in H$_2$SO$_4$ solution, while the MnO$_2$ powders were left as deposits. Several parameters, i.e., H$_2$SO$_4$ concentrations, temperature, time, and liquid/solid (L/S) ratio, are related with the leaching operation. As a simplified means of performing the leaching experiments, equal powder residues were used to react with different H$_2$SO$_4$ solutions, i.e., with different concentrations and volumes, at room temperature. It was indicated that a high L/S ratio, i.e., more than 6, was required when 1 mol L^{-1} H$_2$SO$_4$ solution was used, and the leaching solution had a low Zn^{2+} concentration, which is not favorable for the next electrolytic process. Correspondingly, when the H$_2$SO$_4$ solution with 2 mol L^{-1} or 3 mol L^{-1} concentration was used, the leaching solutions with higher Zn^{2+} concentration could be obtained. The effects of H$_2$SO$_4$ amounts, i.e., the L/S ratio, on the leaching ratio of the powder residues are shown in Fig. 3.

From Fig. 3, it can be seen that the leaching ratio, defined as the ratio between the dissolved residue and the total residue, was enhanced with increasing H$_2$SO$_4$ amounts, and approached their maximum level at a lower L/S ratio when a H$_2$SO$_4$ solution with higher acid concentration was used. The maximum leaching ratio, i.e., ~31%, could be obtained when the L/S ratio approached 3 and 2 for 2 mol L^{-1} and 3 mol L^{-1} H$_2$SO$_4$ solutions, respectively, which is in accord with the component analysis of the spent batteries. The 3 mol L^{-1} H$_2$SO$_4$ solution seems more suitable for the leaching process due to a lower L/S ratio, but a higher Mn^{2+} concentration was detected in the leaching solution than that with 2 mol L^{-1} H$_2$SO$_4$ solution, which will go against the electrodeposition of Zn. Thus, to meet the next electrodepositing requirement for the Zn^{2+} and H$_2$SO$_4$ concentrations in the leaching solution, 2 mol L^{-1} H$_2$SO$_4$ solution and a L/S ratio of 3:1 were chosen to dissolve the powder residues, and then 2 mol L^{-1} H$_2$SO$_4$ and water were successively
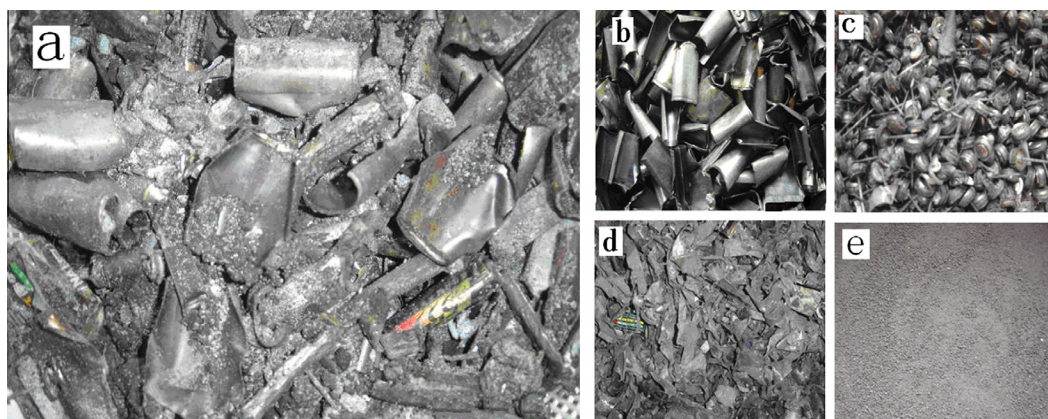
Fig. 2. Digital images of (a) the dismantled substances of spent batteries, (b) the iron cans washed with water, (c) the iron covers and electric rods, (d) the organic separator, label and sealing materials, and (e) the powder residues.
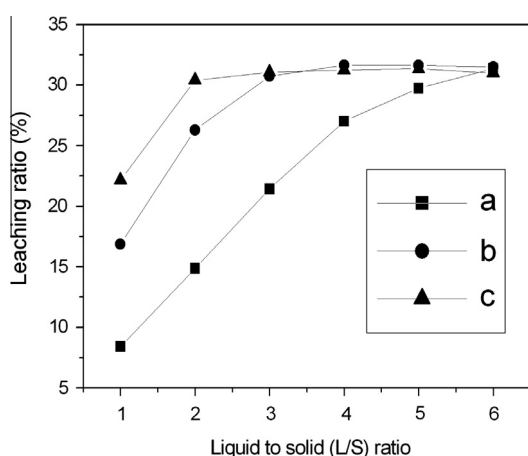

Fig. 3. Leaching ratios of the powder residues under different liquid (H_2SO_4) to solid (powder residues) (L/S) ratios using 1 mol L^{-1} H_2SO_4 (a), 2 mol L^{-1} H_2SO_4 (b), and 3 mol L^{-1} H_2SO_4 (c) at room temperature.

added in the deposit to wash out the remainder zinc. In a experiment of about 0.5 kg powder residues, it was indicated that the little Zn left in the leaching deposit was completely dissolved and washed out, and the washing solution could also be used to adjust the H_2SO_4 content in the final leaching solution to meet the requirement of the electrodepositing operation of Zn. An electrodeposition solution contained 85.8 g L^{-1} Zn^{2+} and almost 20 g L^{-1} H_2SO_4 was finally obtained. The contents of main elements in the leaching solution are presented in Table 1. The elemental contents in the leaching solution validated that the most of Fe, Mn and Cu could be separated in the foregoing treatment, suggesting the pretreatment process was effective.

The Zn^{2+} dissolved in the leaching solution was recovered as metal zinc through the electrodeposition method. The aluminum plate and lead plate were used as the cathodic and anodic electrode of the electrolytic cell, respectively. It is known that a suitable amount of Mn^{2+} in the solution can avoid the potential contamination of the anodic material, i.e., lead, to the purity of the zinc electrodeposited on the cathodic electrode. In fact, some amounts of

Table 1
The contents of the main elements in the leaching solution by using 2 mol L^{-1} H_2SO_4.

Elements	Zn	Mn	Fe	Cu	Pb
Contents (g L^{-1})	85.8	6.7	0.21	0.01	<0.002

Mn^{2+} could be dissolved into the solution based on the discharge level of MnO_2 electrode. Based on the concentrations of zinc (85.8 g L^{-1}) and manganese (6.7 g L^{-1}) presented in Table 1, it is shown that only a fraction of manganese compounds was co-dissolved in the solution during the acidic leaching treatment, which means most of MnO_2 was left in the filtration residue. The current dependence of the cell voltages at different temperatures and cathodic voltages at 40 °C is shown in Fig. 4. The cell voltage was enhanced when a larger current was used, while its value could be decreased with increasing the temperature of electrolytic solution. As a part of the cell, the cathodic voltages at different current densities exhibited similar trend as that of the cell (inset in Fig. 4). In addition, it was observed that the acidic dissolution of the zinc resultant in the cathodic electrode was also increased at higher temperature; in particular, the dissolving reaction would be enhanced dramatically when the temperature exceeded 55 °C. And the electrodeposit in the anodic electrode would disperse into the solution due to the scouring effect of the oxygen gas by-product under the conditions of low temperature and large current densities. Thus, the current density of 300 A m^{-2} and the solution temperature of 37–40 °C were used in the succeeding electrodepositing operation, and the anodic electrode was also surrounded by a glass fiber layer to hinder the dispersing of the electrodeposit.

The electrodepositing parameters and the purity of the electrolytic zinc obtained in the cathodic electrode are presented in Table 2. A high electrolytic efficiency ($\geqslant$85.0%) in the cathodic electrode and the zinc with high purity $\geqslant$99.8% (hereinto, Cu
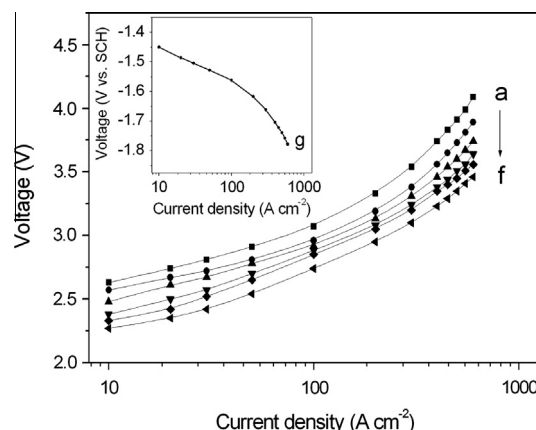

Fig. 4. Current dependence of the cell voltages at (a) 20 °C, (b) 30 °C, (c) 40 °C, (d) 50 °C, (e) 60 °C, (f) 70 °C, and (g) the cathodic voltages at 40 °C.

Table 2
The electrodepositing parameters of electrolytic cell and the purity of electrolytic Zn.

Temperature (°C)	Current density (A m^{-2})	Cell voltage (V)	Cathodic efficiency (%)	Purity of Zn
37–40	300	3.3–3.5	⩾85.0	⩾99.8

0.018%, Fe 0.0014%, Pb 0.009%) were obtained, suggesting that this process is suitable for reclaiming the zinc contained in spent Zn–Mn batteries.

3.3. Reclaiming and reusing manganese compounds

After the separation of the leaching solution using the filtration method, the residue was re-leached with suitable amount of 2 mol L^{-1} H$_2$SO$_4$ and subsequently washed with water to pH = 7 and then dried at 110 °C. The XRD patterns of the powder residue (curve *a*) and the residue after leaching treatment (curve *b*) are shown in Fig. 5. In accordance with the active materials in two electrodes, the diffraction peaks of MnO$_2$, ZnO, and carbon can be observed in curve *a*. The appearance of ZnO diffraction peaks instead of metal Zn is attributed to the oxidation during the separation of iron, organic materials, and electrolyte, and the succeeding washing and drying treatment. The carbon was the conductivity additive of the manganese dioxide electrode, with the low intensity in curve *a* being ascribed to its low content in the powder residue. From curve *b*, it is shown that carbon and MnO$_2$ co-existed in the solid residue after the separation of zinc, and the microstructure of MnO$_2$ was not affected during the battery production and the recycling treatment. However, it was observed that there was difference in the particle size and pile-density between the recovered MnO$_2$ and the commercial electrolytic MnO$_2$, showing the recovered MnO$_2$ is not an eligible raw material in the production of Zn–Mn batteries.

In addition to the MnO$_2$ filtration deposit, the electrolytic MnO$_2$ could also be obtained from the electrolytic reaction on the anodic electrode of the electrolytic cell. Although only ∼5.6% electrolytic efficiency could be obtained due to low Mn^{2+} concentration and electrolytic temperature, the accumulative problem of Mn^{2+} in the electrolytic solution during the electrolytic reaction of zinc was partially avoided. The XRD patterns of the electrolytic MnO$_2$ used in the manufacturing of the battery (curve *a*) and the electrolytic MnO$_2$ obtained on the anodic electrode (curve *b*) are shown in Fig. 6. Compared with curve *a*, besides the diffraction peaks matching to curve *a*, some additional peaks corresponding to the phase of
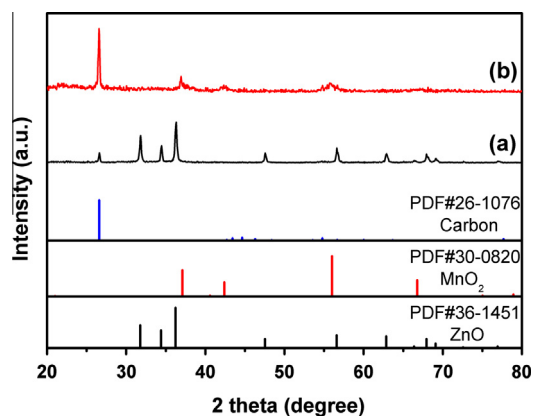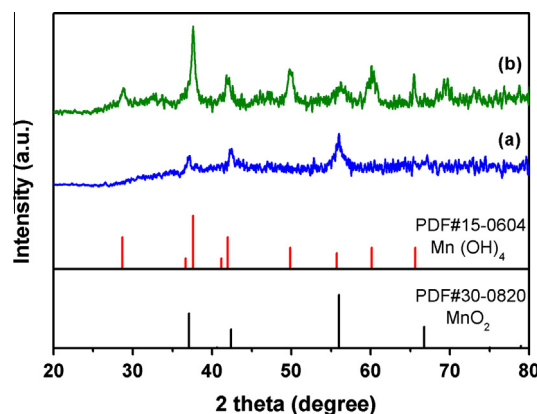

Fig. 6. X-ray diffraction patterns of (a) the electrolytic MnO$_2$ used in the manufacturing of battery and (b) the manganese oxides obtained on anodic electrode.

Mn(OH)$_4$ are also observed, indicating that the products on the anodic electrode are not pure electrolytic MnO$_2$. Namely, the anodic products are electrolytic MnO$_2$ with impurity phase, this impurity phase is primarily ascribed to the by-product during the electrochemical reaction of Mn^{2+} to MnO$_2$.

Because no other metallic elements exist in the recovered MnO$_2$ and electrolytic MnO$_2$, they were used as the manganese source to synthesize the LiNi$_{0.5}$Mn$_{1.5}$O$_4$ electrode material of lithium-ion battery. The recovered manganese materials had smaller particle sizes than the commercial electrolytic MnO$_2$, which favors the use of ball-milling during the mixing step. From the XRD pattern of the as-synthesized LiNi$_{0.5}$Mn$_{1.5}$O$_4$ shown in Fig. 7a, it can be seen that the diffraction peaks are in good agreement with those of the PDF powder diffraction data file No. 32-0851, showing a pure-phase structure that can be obtained using these precursors. The sample exhibits the cubic face-centered spinel structure with a space group of Fd3m, which may exhibit good structural reversibility during the lithiation/delithiation process (Santhanam and Rambabu, 2010). Fig. 7b shows the SEM image of the LiMn$_{1.5}$Ni$_{0.5}$O$_4$; the diameters of these particles are in a range of 2 μm to 12 μm, which leads to a pile-density of 1.9 g cm^{-3} and favors the increase of capacity density per volume. To check the electrochemical performances of the LiNi$_{0.5}$Mn$_{1.5}$O$_4$, the charge–discharge curves are recorded in the potential window of 3.5–4.9 V at the rate of 0.1 °C, as shown in Fig. 7c and d. The discharge voltage plateaus observed at potentials of approximately 4.0 V and 4.7 V corresponding to the Mn^{3+}/Mn^{4+} and Ni^{2+}/Ni^{4+} redox processes, respectively (Deng et al., 2012; Kraytsberg and Ein-Eli, 2012). The charge and discharge capacities are calculated to be 123.4 mAh g^{-1} and 118.3 mAh g^{-1}, respectively. The voltage plateau approximately 4.7 V holds over 88% of the discharge capacity, indicating the as-synthesized sample is an ideal high voltage cathode material. In addition, the capacity still retained 108.6 mAh g^{-1} after 38 cycles (Fig. 7d), which indicates that the LiNi$_{0.5}$Mn$_{1.5}$O$_4$ has good capacity retention upon cycling.

Furthermore, compared to the samples synthesized by using the commercial electrolytic MnO$_2$, a comparable charge–discharge efficiency and cycle performance was obtained, demonstrating

Fig. 5. X-ray diffraction patterns of (a) the powder residues indicated in Fig. 2e and (b) the residue after the separation of leaching solution.
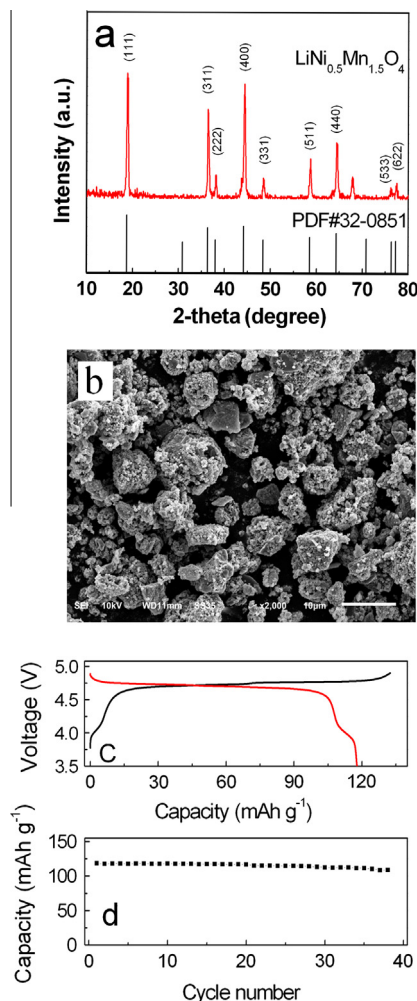
Fig. 7. (a) XRD pattern, (b) SEM image, (c and d) charge–discharge curves and cycle performance at 0.1 °C of the LiNi$_{0.5}$Mn$_{1.5}$O$_4$ sample.

the feasibility of the recovered manganese compounds as manganese source to produce the LiNi$_{0.5}$Mn$_{1.5}$O$_4$ battery material. As mentioned above, due to the unpredicted particle size and pile-density of the recovered MnO$_2$ and electrolytic MnO$_2$, it is difficult to utilize them as the commercial electrolytic MnO$_2$ in the products, but the elemental purity of these recovered manganese oxides demonstrates they are suitable raw material to produce manganese-contained products.

4. Conclusions

In summary, a facile method for the reclaiming the spent alkaline Zn-Mn batteries from the manufacturing batteries to prepare valuable materials, i.e., electrolytic Zn and LiMn$_{1.5}$Ni$_{0.5}$O$_4$ battery material, was proposed and optimized. The experimental results demonstrated that target Zn and manganese valuable materials, and iron, electrolyte and organic materials could be reclaimed. Hereinto, the zinc contained in the dismantled substances was dissolved into H$_2$SO$_4$ solution and then electrodeposited as metal Zn with high purity. In addition, the recovered manganese oxides were used as the manganese source to synthesize LiNi$_{0.5}$Mn$_{1.5}$O$_4$ electrode material of lithium-ion batteries, which exhibited comparable electrochemical performances as the sample synthesized by using the commercial electrolytic MnO$_2$. The proposed process

is environmentally acceptable and is applicable for Zn–Mn battery factories to recycle their spent batteries.

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